ELSEVIER

Journal of Organometallic Chemistry 585 (1999) 106–114

Journal of Organo metallic Chemistry

The structure of bicyclic ferrocenylmethylene substituted 2-pyrazolines and their reactions with azodicarboxylic acid *N*-phenylimide

Elena I. Klimova [a,*], Marcos Martínez García [b], Tatiana Klimova Berestneva [a], Cecilio Alvarez Toledano [b], Ruben Alfredo Toskano [b], Lena Ruíz Ramírez [a]

[a] *Universidad Nacional Autónoma de México (UNAM), Facultad de Química, Circuito Interior, Ciudad Universitaria, Coyoacán, C.P. 04510, México D.F., Mexico*

[b] *Universidad Nacional Autónoma de México (UNAM), Instituto de Química, Circuito Exterior, Ciudad Universitaria, Coyoacán C.P. 04510, México D.F., Mexico*

Received 9 February 1999; received in revised form 8 April 1999

Abstract

Asymmetrical induction in the synthesis of bicyclic pyrazolines with a ferrocenyl substituent has been studied. A relatively high diastereomeric selectivity in the 'chiral-center-by-a-chiral-center' induction of the 1,2-type has been observed. Molecular geometry of a *cis*-diastereomer of 1-acetyl-9-ferrocenyl-4-ferrocenylmethylene-1,2-diazabicyclo[4.3.0]non-2-ene has been established. Bicyclic 2-pyrazolines having conjugated ferrocenylmethylene fragments interact with azodicarboxylic acid *N*-phenylimide to form diene and monoene adducts. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: [4 + 2]-Cycloaddition; Diastereomeric selectivity; Ferrocene; Induction; Molecular structure; Monoene addition; Pyrazoline; *S-cis*-Hetero-1,3-dienes; X-ray structural analysis

1. Introduction

At present we observe an increasing interest in the diastereoselective synthesis as a method of preparation of pure diastereomers. This interest is justified basically by the practical needs of the pharmaceutical industry for the production of large amounts of physiologically active compounds [1–3]. It has been established that compounds having ferrocenyl substituents frequently manifest biological activity. For example, ferrocenyl substituted cyclopropanes, cyclohexenes and tetrahydrophthalates manifest anti-inflammatory [4–6], analgesic [6,7] and antiviral properties [4]. This effect is different for the various diastereomeric and enantiomeric forms of one and the same compound. Therefore, it is of interest to study the stereochemical aspects of the synthesis of compounds having ferrocenyl fragments with potential biological activity.

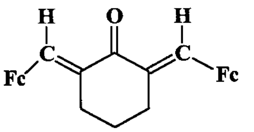
It is also known that the presence of a ferrocenyl substituent in the molecules has an asymmetric effect [8–10]. For example, 1,3- and 1,1-asymmetric induction ('chiral-center-by-a-chiral-plane' and vice versa) have been observed [11] in the formation of 2-pyrazolines with ferrocenyl and phenylbutadienylirontricarbonyl substituents at positions 3 and 5 of the pyrazoline ring. High diastereomeric selectivity is inherent in the synthesis of 2-pyrazolines. Other information on the stereochemistry of formation of 2-pyrazolines with a ferrocene group is virtually lacking. The present study has been undertaken with the aim at determining the stereochemistry of formation of bicyclic pyrazolines with conjugated ferrocenylmethylene fragments and the possibility of the use of these systems as *S-cis*-hetero-1,3-dienes.

* Corresponding author. Fax: + 52-5-6225366.
E-mail address: kilmova@servidor.unam.mx (E.I. Klimova)

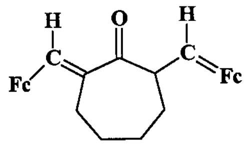
PII: S0022-328X(99)00202-8

2. Results and discussion

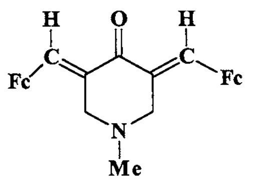
Bis(ferrocenylmethylene)cycloalkanones **1** and **2** and bis(ferrocenylmethylene)piperidones **3** and **4** were used as the starting compounds in the synthesis of 2-pyrazolines.



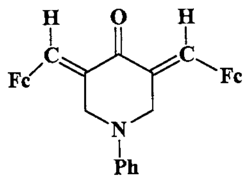
1



2



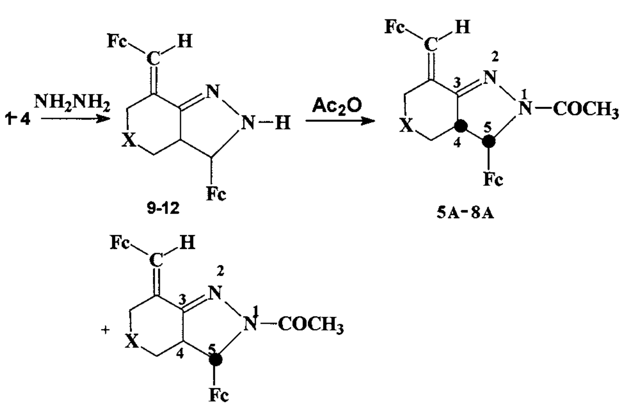
3



4

The α,β-unsaturated carbonyl compounds **1**–**4** are accessible through condensation of ferrocenecarbaldehyde with the corresponding cyclic ketones in the presence of base (NaOH, Bu^{t}OK). These compounds were isolated mainly as single (*E*,*E*)-isomers with bulky ferrocene fragments oriented 'outwardly' with respect to the *S*-*cis*-dienone systems [12,13]. The ^{1}H-NMR spectroscopy data for compounds **1**–**4** are listed in Table 1.

1-Acetyl-2-pyrazolines **5**–**8** were obtained from chalcones **1**–**4** by addition of hydrazine [11,14] followed by acetylation of unstable secondary nitrogen intermediates **9**–**12**:



X = CH$_2$ (5,9); (CH$_2$)$_2$ (6,10); NMe (7,11); NPh (8,12)

An analysis of the ^{1}H-NMR spectra of the products **5**–**8** obtained (Table 1) has shown that all the pyrazolines represented are mixtures of two diastereomeric forms A and B in different proportions, but with prevalence of one form (A). Thus, in this case the 'chiral-center-by-a-chiral-center' asymmetric induction of the 1,2-type has been realized [10]. Table 2 lists the effect of chiral elements in the starting chalcones on the diastereoselectivity of pyrazoline formation.

According to the ^{1}H-NMR data, the chemical shifts for the H(5) protons of the pyrazoline rings of the bicyclic pyrazolines **5**A–**8**A obtained are similar (δ 4.86, 4.97, 4.84 and 5.02, respectively); $^3J_{H(4),H(5)}$ coupling constant values are also similar with the exception of the cycloheptane derivative **6**A (6.4, 2.7, 6.8 and 7.6 Hz). The analogous protons in the B-diastereomers resonate at lower fields (δ 5.53, 5.44, 5.32 and 5.58, respectively) and the ^3J coupling constants are larger (9.3, 11.8, 9.2 and 9.6 Hz).

Thus, one may suggest that the H(4) and H(5) atoms in the pyrazoline rings are *cis* oriented in the A-diastereomers and *trans* oriented in B-diastereomers.

We managed to isolate individual isomers **5**A–**8**A and **5**B–**8**B by multiple crystallization and preparative TLC on alumina. The yields of pure isomers, their melting points, and elemental analysis data are given in Table 3, and Table 4 presents their ^{13}C-NMR spectral data.

The independent structural determination for pyrazoline **5**A has been performed by X-ray analysis. The general view of the molecule **5**A is shown in Fig. 1. The pivotal element of the molecule **5**A is the bicyclic framework of a five-membered pyrazoline in the form of a flattened envelope fused with a six-membered carbocycle. The ferrocenyl substituent occupies a pseudoaxial position. The hydrogen atom H(4) at C(3a) and the ferrocenyl substituent at C(3) are *trans* oriented relative to the 5-membered cycle, while the hydrogen atoms H(4) at C(3a) and H(5) at C(3) are *cis* oriented.

The N(1)=C(7a) bond on the pyrazoline ring is somewhat longer, and the N(1)–N(2) bond is somewhat shorter compared to the standard lengths (cf. *d* (C=N) 1.23 Å [11] and *d*(N–N) 1.45 Å [11]). The *E*-configuration of the ferrocenylmethylene fragment in the starting chalcone has been retained. The Fe–C and C–C bond lengths and the geometry of the ferrocenyl sandwiches in the isomer **5**A have ordinary parameters.

On the basis of the X-ray structural analysis of pyrazoline **5**A and ^{1}H-NMR data for all the diastereomeric compounds (**5**A–**8**A and **5**B–**8**B), the structures with pseudoequatorial orientations of the H(4) and H(5) atoms of the pyrazoline rings and pseudoaxial positions of ferrocenyl substituents were as-

Table 1
^{1}H-NMR spectral data of compounds **2**; **3**; **4**; **5**A,B; **5**A,B; **6**A,B; **7**A,B; **8**A,B; **13**a,b; **14**a,b; **15**a,b**;** **16**a,b; **17**; **18**; **19** and **20** (δ, J (Hz))

Compound	C_5H_5	C_5H_4	CH_2	Fc–CH	CH	CH_3, Ar, NH
2	4.16 s (10H)	4.38 m (4H), 4.53 m (4H)	1.94 m (4H), 2.60 m (4H)	–	7.14 s (2H)	–
3	4.18 s (10H)	4.46 m (4H), 4.49 m (4H)	3.61 m (4H), $J=1.36$	–	7.61 s (2H)	2.53 s (3H)
4	4.19 s (10H)	4.47 m (4H), 4.48 m (4H)	2.90 m (2H), 3.73 m (2H)	–	7.64 s (2H)	7.30 m (5H)
5A	4.15 s (5H), 4.17 s (5H)	4.16 m (3H), 4.30 m (1H), 4.32 m (1H), 4.35 m (1H), 4.40 m (1H), 4.43 m (1H)	1.66 m (2H), 2.20 m (2H), 3.0–3.15 m (2H)	4.89 d (1H), $J=$ 6.4	3.40 m (1H), 6.80 d (1H), $J=1.8$	2.33 s (3H)
5B	4.15 s (5H), 4.24 s (5H)	3.85–4.25 m (8H)	1.02 m (2H), 1.75 m (2H), 2.30 m (2H)	5.53 d (1H), $J=$ 9.3	3.38 m (1H), 7.12 d (1H), $J=1.4$	2.46 s (3H)
6A	4.195 s (5H), 4.199 s (5H)	4.00 m (1H), 4.15 m (2H), 4.36 m (2H), 4.46 m (3H)	1.20 m (1H), 1.72 m (2H), 2.15 m (4H), 3.32 m (1H)	4.97 d (1H), $J=$ 2.7	3.49 m (1H), $J=2.75$, 7.19 d (1H), $J=1.6$	2.35 s (3H)
6B	4.20 s (5H), 4.26 s (5H)	3.92 m (2H), 3.98 m (2H), 4.10 m (2H), 4.38 m (2H)	1.38 m (1H), 1.80 m (2H), 2.40 m (4H), 3.11 m (1H)	5.44 d (1H), $J=$ 11.8	3.62 m (1H), 6.86 bs (1H)	2.20 s (3H)
7A	4.15 s (5H), 4.18 s (5H)	4.29 m (2H), 4.34 m (4H), 4.38 m (2H)	2.42 m (1H), 2.92 m (1H), 3.22 m (1H), 3.75 m (1H)	4.84 d (1H), $J=$ 6.8	4.10 m (1H), 6.86 d (1H), $J=1.2$	2.32 s (3H), 2.49 s (3H)
7B	4.17 m (5H), 4.25 m (5H)	4.02 m (2H), 4.07 m (2H), 4.18 m (2H), 4.29 m (2H)	2.28 m (1H), 3.06 m (1H), 3.36 m (1H), 3.84 m (1H)	5.32 d (1H), $J=$ 9.24	4.13 m (1H), 7.09 d (1H), $J=0.9$	2.46 s (3H), 2.50 s (3H)
8A	4.12 s (5H), 4.23 s (5H)	4.10 m (2H), 4.14 m (2H), 4.19 m (2H), 4.30 m (2H)	2.59 m (1H), 2.89 m (1H), 3.09 m (2H)	5.09 d (1H), $J=$ 7.6	4.18 m (1H), $J=7.6$ 7.15 bs (1H)	2.41 s (3H), 7.21 m (5H)
8B	4.16 s (5H), 4.23 s (5H)	3.97 m (2H), 4.13 m (2H), 4.31–4.36 m (4H)	2.69–2.80 m (2H), 2.89 m (1H), 3.38 m (1H)	5.58 d (1H), $J=$ 9.6	4.16 m (1H), 7.18 d (1H), $J=1.2$	2.45 s (3H), 7.20–7.35 m (5H)
13a	4.13 s (5H), 4.24 s (5H)	4.07 m (2H), 4.17 m (2H), 4.20 m (2H), 4.32 m (2H)	1.73 m (2H), 2.30 m (2H), 2.52 m (2H)	4.84 d (1H), $J=$ 6.9, 6.31 bs (1H)	4.22 m (1H), $J=4.5$, 6.9	2.18 s (3H), 7.34–7.50 m (5H)
13b	4.12 s (5H), 4.23 s (5H)	4.14 m (2H), 4.18 m (2H), 4.25 m (2H), 4.30 m (2H)	1.95 m (2H), 2.20 m (2H), 2.48 m (2H)	4.39 d (1H), $J=$ 4.3, 6.18 s (1H)	3.58 m (1H), $J=4.3$, 8.1	2.17 s (3H), 7.45 m (5H)
14a	4.13 s (5H), 4.25 s (5H)	3.64 m (2H), 4.05 m (2H), 4.46 m (2H), 4.62 m (2H)	1.85 m (4H), 2.40 m (4H)	4.92 d (1H), $J=$ 3.3, 6.45 bs (1H)	3.68 m (1H), $J=3.3$, 7.6	2.13 s (3H), 7.30–7.50 m (5H)
14b	4.14 s (5H), 4.20 s (5H)	4.15 m (2H), 4.18 m (2H), 4.24 m (4H)	1.89 m (4H), 2.25 m (4H)	4.175 d (1H), $J=$ 3.8, 6.27 bs (1H)	3.42 m (1H), $J=3.8$	2.01 s (3H), 7.36 m (5H)
15a	4.11 s (5H), 4.26 s (5H)	4.01 m (2H), 4.09 m (2H), 4.13 m (2H), 4.45 m (2H)	2.64 m (2H), 3.31 m (2H)	4.98 d (1H), $J=$ 4.0, 6.56 s (1H)	4.06 m (1H), $J=4.02$	2.28 s (3H), 2.44 s (3H), 7.28–7.58 m (5H)

Table 1 (continued)

15b	0.00 (00H)	4.19 m (2H), 4.30 m (2H),	2.88 m (2H), 3.81 m (2H)	4.80 d (1H), *J* =	3.89 m (1H), 6.85 s (1H)	1.98 s (3H), 7.30–7.49 m (10H)
15b	4.23 s (5H), 4.28s (5H)	4.19 m (2H), 4.30 m (2H), 4.42 m (2H), 4.50 m (2H)	2.88 m (2H), 3.81 m (2H)	4.69 d (1H), *J* = 6.3, 5.99 s (1H)	3.94 m (1H), *J* = 6.3	2.19 s (3H), 2.31 s (3H), 7.37 m (5H)
16a	4.12 s (5H), 4.30 s (5H)	4.03 m (2H), 4.13 m (2H), 4.15 m (2H), 4.61 m (2H)	2.95 m (2H), 3.48 m (2H)	5.08 d (1H), *J* = 2.4, 6.92 s (1H)	4.11 m (1H), *J* = 2.45	2.21 s (3H), 7.14–7.60 m (10H)
16b	4.19 s (5H), 4.28 s (5H)	4.11 m (2H), 4.14 m (2H), 4.18 m (2H), 4.35 m (2H)	3.20 m (2H), 3.65 m (2H)	4.80 d (1H), *J* = 7.8, 6.05 s (1H)	4.01 m (1H), *J* = 7.8	1.98 s (3H), 7.30–7.49 m (10H)
17	4.11 s (5H), 4.24 s (5H)	4.08 m (1H), 4.16 m (1H), 4.21 m (4H), 4.31 m (1H), 4.38 m (1H)	1.75 m (1H), 2.24 m (1H), 2.60 m (2H)	4.85 d (1H), *J* = 7.0, 6.16 s (1H)	3.55 m (1H), 6.30 t (1H), *J* = 6.7	2.19 s (3H), 7.36–7.60 m (5H), 9.30 bs (1H)
18	4.14 s (5H), 4.26 s (5H)	4.00 m (1H), 4.14 m (1H), 4.19 m (4H), 4.25 m (1H), 4.48 m (1H)	1.67 m (2H), 1.80 m (2H), 2.51 m (2H)	4.91 d (1H), *J* = 3.6, 6.21 s (1H)	3.40 m (1H), 6.48 t (1H), *J* = 6.4	2.14 s (3H), 7.30–7.45 m (5H), 8.91 bs (1H)
19	4.16 s (5H), 4.27 s (5H)	4.08 m (1H), 4.17 m (1H), 4.19 m (4H), 4.43 m (1H), 4.58 m (1H)	2.95 m (2H)	5.03 d (1H), *J* = 3.9, 6.08 s (1H)	3.90 m (1H), 6.90 s (1H)	2.17 s (3H), 2.30 s (3H), 7.38 m (5H), 9.89 s (1H)
20	4.18 s (5H), 4.27 s (5H)	4.01 m (1H), 4.10 m (1H), 4.12 m (4H), 4.45 m (1H), 4.61 m (1H)	2.93 m (2H)	5.12 d (1H), *J* = 2.9, 6.03 s (1H)	3.89 m (1H), 6.85 s (1H)	2.18 s (3H), 7.15–7.45 m (10H), 9.96 s (1H)

Table 2
The degree of asymmetric induction in the synthesis of ferrocenylpyrazolines

Induction path	Induction variant	Induction type	Yield (%) of diastereomers [a]		Diastereomeric selectivity (%)
			A	B	
1 → 5	Center → center	1,2	80	20	60
2 → 6	Center → center	1,2	90	10	80
3 → 7	Center → center	1,2	95	5	90
4 → 8	Center → center	1,2	65	35	30

[a] Yields of the reaction products were calculated on the basis of ^{1}H-NMR spectral data.

Table 3
Yields, melting point and elemental analysis data for the synthesized compounds

Compound	Yield (%)	M.p. (°C)	Molecular formula	Found (%)				Calculated (%)			
				C	H	Fe	N	C	H	Fe	N
2	46	177–178	$C_{29}H_{28}Fe_2O$	68.87	5.73	22.31	–	69.08	5.60	22.15	–
3	73	197–198	$C_{28}H_{27}Fe_2NO$	66.74	5.21	22.35	2.58	66.56	5.39	22.11	2.77
4	66	193–194	$C_{33}H_{29}Fe_2NO$	70.07	4.94	19.78	2.31	69.87	5.15	19.69	2.47
5A	68	187–188	$C_{30}H_{30}Fe_2N_2O$	65.73	5.33	20.57	5.28	65.96	5.53	20.45	5.13
5B	12	197–198	$C_{30}H_{30}Fe_2N_2O$	66.11	5.27	20.63	5.01	65.96	5.53	20.45	5.13
6A	72	209–210	$C_{31}H_{32}Fe_2N_2O$	66.63	5.57	19.73	4.71	66.45	5.76	19.94	5.00
6B	8	186–187	$C_{31}H_{32}Fe_2N_2O$	66.27	5.92	20.10	5.03	66.45	5.76	19.94	5.00
7A	82	159–160	$C_{30}H_{31}Fe_2N_3O$	64.37	5.26	19.73	7.24	64.20	5.57	19.90	7.48
7B	2.5	181–182	$C_{30}H_{31}Fe_2N_3O$	64.11	5.63	20.07	7.41	64.20	5.57	19.90	7.48
8A	58	165–166	$C_{35}H_{33}Fe_2N_3O$	67.22	5.52	18.17	6.85	67.44	5.34	17.92	6.74
8B	27	189–190	$C_{35}H_{33}Fe_2N_3O$	67.18	5.18	18.09	6.59	67.44	5.34	17.92	6.74
13a	48	164–165	$C_{38}H_{35}Fe_2N_5O_3$	63.48	5.03	15.37	9.81	63.27	4.89	15.49	9.70
13b	10	176–177	$C_{38}H_{35}Fe_2N_5O_3$	63.12	4.74	15.63	9.58	63.27	4.89	15.49	9.70
14a	34	188–189	$C_{39}H_{37}Fe_2N_5O_3$	63.78	4.82	15.42	9.71	63.69	5.07	15.20	9.52
14b	11	214–215	$C_{39}H_{37}Fe_2N_5O_3$	63.43	5.28	15.03	9.33	63.69	5.07	15.20	9.52
15a	37	168–169	$C_{38}H_{36}Fe_2N_6O_3$	62.15	5.12	14.98	11.63	61.98	4.93	15.17	11.41
15b	8	192–193	$C_{38}H_{36}Fe_2N_6O_3$	61.82	5.17	15.28	11.31	61.98	4.93	15.17	11.41
16a	30	173–174	$C_{43}H_{38}Fe_2N_6O_3$	64.85	4.71	13.76	10.67	64.68	4.80	14.00	10.52
16b	9	203–205	$C_{43}H_{38}Fe_2N_6O_3$	64.53	4.99	14.22	10.41	64.68	4.80	14.00	10.52
17	20	193–194	$C_{38}H_{35}Fe_2N_5O_3$	63.51	4.68	15.71	9.63	63.27	4.89	15.49	9.70
18	31	203–205	$C_{39}H_{37}Fe_2N_5O_3$	63.81	5.33	15.01	9.68	63.69	5.07	15.20	9.52
19	34	216–217	$C_{38}H_{36}Fe_2N_6O_3$	62.03	4.87	15.01	11.60	61.98	4.93	15.17	11.41
20	43	221–222	$C_{43}H_{38}Fe_2N_6O_3$	64.77	5.03	13.84	10.32	64.68	4.80	14.00	10.52

cribed to A-diastereomers. B-diastereomers were referred to as *trans* isomers, where the H(4) hydrogen atoms and ferrocenyl substituents are pseudoequatorial, and the H(5) hydrogen atoms occupy pseudoaxial positions. In our opinion, the *E*-configuration of the ferrocenylmethylene fragments has been conserved.

We established that bicyclic 1-acetyl-2-pyrazolines with ferrocenylmethylene substituents in conjugated position relative to the N(2) pyrazoline cycle (**5**A–**8**A) react with azodicarboxylic acid *N*-phenylimide [14] at 0°C, forming the adducts **13**–**16**-[4 + 2]-cycloaddition reactions. Besides, we separated from the reaction mixture compounds **17**–**20**, as products of a monoenic addition reaction.

Table 4
^{13}C-NMR spectral data of the synthesized compounds (δ)

Group	**5**A	**5**B	**6**A	**6**B	**7**A	**8**A	**13**a	**13**b	**14**a	**14**b
C_5H_5	68.25 69.22	69.25 69.37	68.30 69.22	69.30 69.75	68.30 69.29	69.32 69.41	68.27 69.14	68.29 69.13	68.18 69.22	68.18 69.22
C_5H_4	66.48 67.96 68.07 69.26 69.42 69,72 69.73 70.55	65.43 66.52 67.07 67.38 67.86 69.27 69.50 70.84	65.78 68.78 68.15 69.34 69.40 69.81 69.93 69.98	64.67 65.83 66.24 68.30 69.11 69.48 71.04 72.01	66.69 68.06 68.21 68.28 69.64 69.75 69.89 70.60	65.58 66.05 67.23 67.68 68.56 69.75 69.78 70.92	67.66 68.03 68.22 68.39 68.40 68.45 68.61 70.48	67.64 68.00 68.20 68.27 68.35 68.44 68.60 70.48	67.45 68.11 68.16 68.39 68.45 68.50 68.51 70.82	67.44 68.12 68.35 68.38 68.44 68.50 68.56 70.82
C_{ipso}Fc	80.40 88.67	80.23 85.99	80.93 87.44	79.96 91.19	79.56 88.12	79.96 85.60	84.37 87.59	84.36 87.60	85.61 86.37	85.61 86.38
CH=	125.93	126.20	127.45	126.02	128.30	126.60	-	-	-	-
CH_3	31.29	29.22	30.50	29.00	22.50 45.84	41.98	30.89	30.90	31.70	30.69
CH_2	22.32 24.57 27.82	21.95 23.45 24.64	21.84 28.76 29.92 35.70	21.80 26.12 28.83 34.78	57.14 58.85	51.60 57.82	22.62 26.43 28.46	22.61 26.42 28.45	22.19 25.37 25.38 27.67	22.19 25.37 25.39 27.67
CHFc	61.14	58.76	62.94	62.98	59.49	59.66	57.77 65.97	60.71 65.98	59.72 65.50	59.72 62.56
CH	55.12	50.24	54.84	54.42	53.73	54.15	52.54	52.55	54.21	54.21
C	127.20	127.95	130.34	130.27	126.02	132.60	131.42 139.52	131.42 139.53	133.98 143.42	133.99 143.42
C=O	170.15	167.75	168.57	169.24	170.61	174.12	155.10 168.20 169.48	155.09 168.01 169.49	156.84 156.85 168.41	156.84 168.41 170.20
C=N	159.46	159.69	161.40	161.43	156.40	158.03	–	–	–	–
Ar	–	–	–	–	–	127.8 128.4 128.6 140.05	125.4 128.2 129.0 130.6 152.53	128.0 128.2 129.0 130.6 151.55	125.6 128.1 129.1 131.3 152.36	125.6 128.3 129.1 131.3 151.30

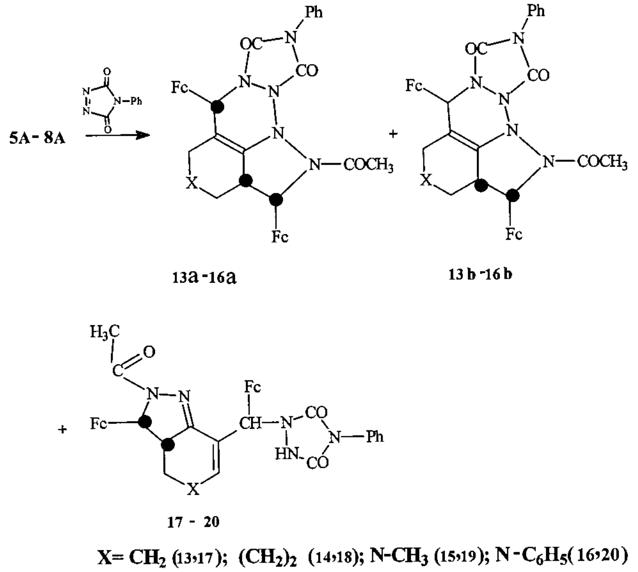


Table 5
Crystal data, data collection and refinement parameters for **5**A

Data	**5**A
Molecular formula	$C_{30}H_{30}Fe_2N_2O$
Formula weight (g mol^{-1})	546.26
Temperature (K)	293
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	10.403(1)
b (Å)	20.605(1)
c (Å)	11.494(1)
α (°)	90.0
β (°)	90.55(1)
γ (°)	90.0
V (Å^3)	2463.7(3)
Z	4
D_{calc} (Mg m^{-3})	1.473
Absorption coefficient (mm^{-1})	9.639
F(000)	1136
Radiation, λ (Å)	Cu–K$_\alpha$, 1.54178
Monochromator	Graphite
Θ range (°)	$1.50 < \Theta < 56.75$
Reflections collected	4195
Reflections independent	3289
R_{int}	0.0630
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0631$, [a] $wR_2 = 0.1350$
R indices (all data)	$R_1 = 0.1112$, [a] $wR_2 = 0.1577$
Data/restraints/parameters	3289/0/317
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit	1.007
Min./max. residual electron density (e Å^{-3})	−0.403/0.643
Hydrogen atoms	Riding

[a] Weighting scheme: $w = [\sigma^2(F_o^2) + (0.0605P)^2 + 3.8592P]^{-1}$ where $P = (F_o^2 + 2F_c^2)/3$.

The $[4+2]$-cycloaddition occurs stereoselectively. The adducts **13**–**16** were obtained as mixtures of *endo* (**13**a–**16**a) and *exo* (**13**b–**16**b) isomers, where the preponderant isomers possess presumably *endo* conformation. This could be inferred from the [1]H-NMR spectral data (Table 1): **13**a:**13**b = 4:1, **14**a:**14**b = 3.5:1, **15**a:**15**b = 5:1, and **16**a:**16**b = 4:1.

The assignment of either *endo* or *exo* structures to **13**a–**16**a and **13**b–**16**b, respectively, was given according to the previously found criteria for distinguishing *endo* and *exo* isomers of $[4+2]$-cycloadducts with ferrocene substituents [15,16]. Thus the signals for the protons of the C_5H_4 groups of the ferrocenyl fragments at position 5 in compounds **13**a–**16**a are shifted upfield compared to the singlets for the protons of the C_5H_5 groups of the same substituents, which should not take place for the *exo* isomers **13**b–**16**b, and this is the case indeed.

The *endo* isomers **13**a–**16**a could be isolated as individual compounds by crystallization from ethanol. However, our attempts to determine their spatial structures by X-ray analysis have failed so far.

The *exo* adducts **13**b–**16**b and compounds **17**–**20** were isolated by TLC on alumina. The [1]H- and [13]C-NMR spectra of the obtained compounds are listed in Tables 1 and 4.

3. Experimental

All [1]H- and [13]C-NMR spectra were recorded on a Unity Inova Varian spectrometer (300 and 75 MHz) in $CDCl_3$ solutions with Me_4Si as an internal standard. Unit cell parameters and intensities of reflections were measured on a Siemens P4/Pc diffractometer. The crystallographic data, parameters of the X-ray experiment, and refinements for **5**A are listed in Table 5.

*3.1. Chalcones **1**, **3** and **4***

Synthesized from the corresponding ketones and ferrocenecarbaldehyde in aqueous–ethanolic alkali [16]. Bis(ferrocenylmethylene)cycloheptanone **2** was obtained by refluxing the reactants in toluene in the presence of Bu^{t}OK.

*3.2. Pyrazolines **9**–**12** and **5**–**8***

Chalcones **1**–**4** were converted into pyrazolines **9**–**12** by a conventional procedure, viz., by reaction with hydrazine hydrate in ethanol [11]. Treatment of dry compounds **9**–**12** with acetic anhydride afforded 1-acetyl-derivatives **5**–**8**. Pure isomers **5**A–**8**A were isolated by crystallization from ethanol. Mother liquors were subjected to TLC on alumina (Brockmann activity

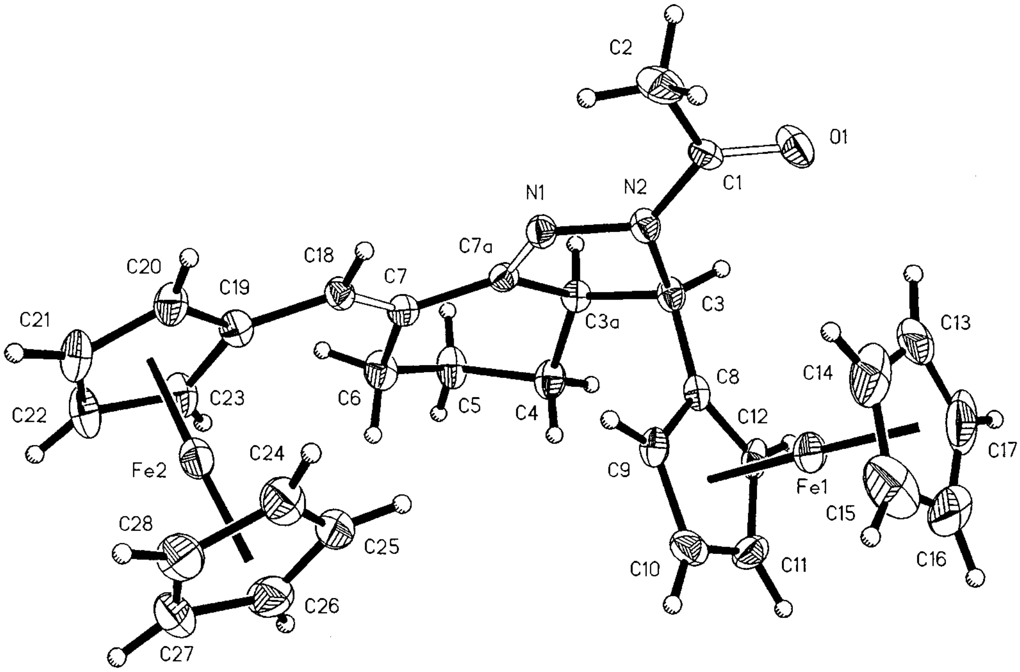


Fig. 1. Crystal structure of **5A**. Selected bond lengths (Å): N(1)–N(2) = 1.412(7); N(2)–C(3) = 1.487(8); N(1)–C(7A) = 1.298(8); N(2)–C(1) = 1.344(8). Selected bond angles (°): C(7A)–N(1)–N(2) = 106.8(5); C(1)–N(2)–C(3) = 126.6(6); C(1)–N(2)–N(1) = 122.1(6); N(1)–N(2)–C(3) = 110.9(5); N(2)–C(3)–C(3A) = 99.0(5).

III, hexane–benzene, 1:1), which made it possible to separate diastereomers **5**A–**8**A and **5**B–**8**B: **5**A R_f = 0.45; **5**B R_f = 0.64; **6**A R_f = 0.53; **6**B R_f = 0.67; **7**A R_f = 0.36; **7**B R_f = 0.44; **8**A R_f = 0.32; **5**B R_f = 0.40.

*3.3. Reaction of pyrazoline **5**A with azodicarboxylic acid N-phenylimide*

Azodicarboxylic acid *N*-phenylimide (0.35 g, 2 mmol) was added at 0°C with stirring to a solution of pyrazoline **5**A (1.10 g, 2 mmol) in 50 ml of acetone. The mixture was stirred at 0°C until the bright color disappeared completely (ca. 3 h), and the solvent was evaporated in vacuo. The residue was recrystallized twice from ethanol to give 0.43 g (30%) of the *endo*-2-acetyl-1,5-diferrocenyl-2a,3,4,5,6,7,8,8a-octahydro-2,2a,3,4-tetraazaacenaphthene-3,4-dicarboxylic acid *N*-phenylimide **13**a. The mother liquors were combined, concentrated in vacuo, and the residue was subjected to TLC on alumina (Brockmann activity III, hexane–ethyl acetate, 2:1) to afford 0.12 g (10%) of the *exo* isomer **13**b, R_f = 0.65, 0.25 g (18%) of **13**a, R_f = 0.53, and 0.3 g (20%) of compound **17**, R_f = 0.41.

Compounds **14**a (R_f = 0.58), **14**b (R_f = 0.65), **15**a (R_f = 0.48), **15**b (R_f = 0.55), **16**a (R_f = 0.42), **16**b (R_f = 0.53), **18** (R_f = 0.35), **19** (R_f = 0.30) and **20** (R_f = 0.28) were synthesized and separated analogously. The yields, melting points, and data from the elemental analyses for the obtained substances are listed in Table 3.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 115494 for 1-acetyl-9-ferrocenyl-4-ferrocenylmethylene-1,2-diazabicyclo[4.3.0.]-non-2-ene **5**A. Copies of this information may be obtained free of charge from The Director, CCDC, 12, Union Road, Cambridge CB2 1EZ (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Financial support from CONACyT (Mexico) is gratefully acknowledged. We would like to thank Oscar Salvador Yañez Muñoz for ^{1}H- and ^{13}C-NMR spectra.

References

[1] T. Hayashi, Pure Appl. Chem. 60 (1998) 7.
[2] M. Sawamura, Y. Ito, Chem. Rev. 92 (1992) 857.
[3] J. Spencer, V. Gramlich, R. Häusel, A. Togni, Tetrahedron Asymmetry 7 (1996) 41.
[4] E.I. Klimova, L. Ruíz Ramírez, M. Martínez García, R.G. Espinosa, N.N. Meleshonkova, Izv. AN SSSR Ser. Khim. 11 (1996) 2743.

[5] E.I. Klimova, V.N. Postnov, N.N. Meleshonkova, A.S. Zaks, V.V. Yushkov, Khim. Farm. Zh. 26 (1992) 69.
[6] E.I. Klimova, V.N. Postnov, N.N. Meleshonkova, A.S. Zaks, E.M. Chukichev, Khim. Farm. Zh. 26 (1992) 34.
[7] E.I. Klimova, V.N. Postnov, N.N. Meleshonkova, M. Martínez García, A.S. Zaks, Khim. Farm. Zh. 28 (1994) 33.
[8] J.W. Scott, D. Valentine, Science 184 (1974) 943.
[9] L.F. Battelle, R. Bau, G.W. Gokel, et al., J. Am. Chem. Soc. 95 (1973) 482.
[10] V.I. Sokolov, L.L. Troitskaya, O.A. Reutov, J. Organomet. Chem. 133 (1977) C28.
[11] A.N. Nesmeyanov, V.A. Sazonova, V.N. Postnov, A.M. Baran, Izv. AN SSSR Ser. Khim. (1979) 902; (1981) 222.
[12] V.N. Postnov, E.I. Klimova, M. Martínez García, N.N. Meleshonkova, V.V. Rybakov, L.A. Aslanov, J. Organomet. Chem. 476 (1994) 189.
[13] E.J. Warawa, J.R. Campbell, J. Org. Chem. 39 (1974) 3511.
[14] E.I. Klimova, L. Ruíz Ramírez, M. Martínez García, N.N. Meleshonkova, Dokl. Akad. Nauk. 351 (1996) 494.
[15] A.N. Chekhlov, V.N. Solov'ev, A.N. Pushin, E.I. Klimova, et al., Izv. AN SSSR Ser. Khim. 3 (1986) 701.
[16] A.N. Pushin, E.I. Klimova, V.A. Sazonova, Zh. Obshch. Khim. 57 (1987) 1102.